COPOLYMERIZATION OF STYRENE WITH 2-ALKYLBUTADIENES

BY

JACK LELAND REDAVAT WILLIAMS

B.Sc., University of Alberta, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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Introduction

The preparation of a synthetic elastomer with properties equal or superior to those of natural rubber has presented a difficult problem in view of the regular structure of natural rubber. Natural rubber consists of chains of polyisoprene, the monomer units of which are linked together in a *cis* manner by 1,4-addition. The high degree of symmetry of natural rubber causes a unique phenomenon since the melting point of the crystalline fraction in stretched rubber approaches the melting point of straight chain paraffins[1]. Production of synthetic elastomers by diene polymerization introduces the problem of 1,2 and 3,4-addition competing with 1,4-addition. Solomon[1] has predicted that the amount of 1,4-addition decreases as one proceeds down the series: 2,3-dimethylbutadiene, isoprene and butadiene. Studies on the manner of addition of butadiene and isoprene by Kolthoff, Lee and Mairs[2] have shown that substitution of a methyl group for hydrogen in the 2-position of butadiene caused an increase in the amount of 1,4-addition when polymerization was carried out in an emulsion system. Consequently it was of interest to investigate the effect of further substitution in butadiene with methyl and larger alkyl groups upon the amount of 1,4-addition. For this purpose 2-ethylbutadiene, 2-isopropylbutadiene, 2-*n*-amylbutadiene and 2,3-dimethylbutadiene were prepared and polymerized.

Discussion Of Results

Dehydration of 2-ethyl-3-hydroxybutene-1 has been found to yield not the expected 2-ethylbutadiene but its rearrangement product, 3-methylpentadiene-1,3. The diene material produced by this method polymerized slowly in an emulsion system. Pyrolysis of 2-ethyl-3-acetoxybutene-1 produced a

diene which polymerized readily and formed a maleic anhydride adduct that was different from that of 3-methylpentadiene-1,3. This is 2-ethylbutadiene.

The dienes resulting from the dehydration of 2-isopropyl-3-hydroxybutene-1 and 2-*n*-amylhydroxybutene-1 failed to polymerize in an emulsion system while those produced by pyrolysis of 2-isopropyl-3-acetoxybutene-1 and 2-*n*-amyl-3-acetoxybutene-1 did polymerize readily.

The infrared absorption spectograms of the dienes produced by acetate pyrolysis were found to be similar to that of isoprene. It is therefore believed that the dienes produced by acetate pyrolysis are true 2-alkylbutadienes.

In the polymerization of 2-alkylbutadienes it was found necessary to reduce the amount of modifier in the Mutual recipe in order to obtain polymers of intrinsic viscosities close to one. The self-modifying tendency was strongest for 2,3-dimethylbutadiene. Isoprene, 2-ethylbutadiene, 2-isopropylbutadiene and 2-*n*-amylbutadiene copolymerize with styrene in the GR-S recipe at about the same rate. All had less tendency to self-modify than 2,3-dimethylbutadiene.

The presence of impurities on ordinary 2,3-dimethylbutadiene which retard and overmodify the polymerization has been demonstrated by the use of a sample of 2,3-dimethylbutadiene which had been purified through the cyclic-sulfone. Reduction of the modifier concentration in the initial monomer charge failed to produce increased intrinsic viscosities until the modifier concentration was reduced to 0.01 parts per hundred of monomer. In the absence of a mercaptan modifier in the initial monomer charge 2,3-dimethylbutadiene failed to polymerize since the impurities were apparently incapable of producing the initiation step.

The result of 1,4-addition determinations on the polymers of 2-alkylbutadienes indicate that the 2-alkylbutadienes polymerize with approximately eighty-five per cent 1,4-addition which had been previously observed for isoprene[2].

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VITA

The author was born in Edmonton, Alberta, Canada on October 25, 1923. He was educated in the Edmonton Public School System and graduated from Victoria High School in 1942. He entered the University of Alberta in the fall of the same year and was graduated from that institution with the degree of Bachelor of Science in Honors Chemistry in May, 1946. From June of that year to the present he has been enrolled in the Graduate School of the University of Illinois while holding the position of Special Research Assistant in Chemistry, working on the Government Synthetic Rubber Program.

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